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ScienceDirect

Physics Procedia 76 (2015) 11 – 15

Physics Procedia

The 17th International Conference on Luminescence and Optical Spectroscopy of Condensed Matter (ICL2014)

Thermoluminescence of uranyl salts under mechano-destruction

A. A. Tukhbatullin, G. L. Sharipov*

Institute of Petrochemistry and Catalysis RAS, 450075, 141, pr. Oktyabrya, Ufa, Russia

Abstract

The thermoluminescence of the salts $UO_2(NO_3)_2 \cdot 6H_2O$ and $UO_2(ClO_4)_2 \cdot 6H_2O$ that have been previously treated mechanically at 77 K was studied. A maximum was observed in thermoluminescence curve at 80-90 K. The thermoluminescence peak intensity depends on duration of mechanical treatment at 77 K. The trap depth of glow centers has been determined using experimental thermoluminescence curves. The calculated activation energy E_{TL} and frequency factor p_0 were 0.21 eV and 10^{10} s^{-1}, respectively

Peer-review under responsibility of The Organizing Committee of the 17th International Conference on Luminescence and Optical Spectroscopy of Condensed Matter

Keywords: Thermoluminescence, triboluminescence, nitrate and perchlorate uranyl salts;

1. Introduction

Thermoluminescence (TL) is glow previously irradiated by ionizing radiation (e.g. UV light, γ-rays, electron bombardment etc.) and occurs within heating [1]. The glow of crystals under TL is caused by extremely low amounts of impurity (activator) or defects of crystal lattice that create charge traps and luminescent centers. In crystals, during the pre-irradiation at room temperature or lower, the energy accumulates creating charge carriers, i.e. holes in a valence band and electrons in a conduction band. The charge carriers are captured on energy levels, defects or impurities in crystal. The growth of the temperature releases trapped charges and they can recombine. In the TL spectrum, de-excitation peaks can be observed in visible, UV or IR regions [1]. TL is mainly used as a

* Corresponding author. Tel.: +7 347 284 27 50; fax: +7 347 284 27 50.
E-mail address: glus@anrb.ru

Peer-review under responsibility of The Organizing Committee of the 17th International Conference on Luminescence and Optical Spectroscopy of Condensed Matter
doi:10.1016/j.phpro.2015.10.003

dosimetry method of ionizing radiation, as well as for identification of defects in semiconductor technology and laser materials [2, 3].

Traditionally activation of TL is performed by ionized radiation [1-3]. Activation by mechanical effects is described only in some articles [4-6]. However, further researches in this area can afford to develop a thermoluminescent prediction method of various natural destructions. In the present study, the TL of crystals of uranyl salts $UO_2(NO_3)_2 \cdot 6H_2O$ and $UO_2(ClO_4)_2 \cdot 6H_2O$ have been investigated in time of heating process after mechanical treatment.

2. Experimental Section

Mechanical treatment of crystals of nitrate and perchlorate uranyl salts (150-200 mg) was carried out in a steel cylindrical cell with a quartz window at the bottom and four-blade mixer with PTFE tube which was driven by an electric motor (1000 rotation per min) [7-9]. Maintenance of low temperature (77 K) in the cell during the mechanical treatment was performed with another auxiliary cell inserted above and filled with liquid nitrogen.
Evaluation of the TL integral intensity was realized with a special apparatus where detector is photo-multiplier tube PMT-39. Emission spectra were recorded using Aminco-Bowman J4-8202 and Fluorolog-3 (Horiba Jobin Yvon) spectrofluorimeters. Photo-multiplires Hamamatsu R3896 and R928P are light detectors.

3. Results and discussion

Figures 1 and 2 show triboluminescence spectra (emission is obtained from the crystal destruction during the mechanical treatment) of perchlorate and nitrate uranyls obtained at 77 K. Despite the weak luminescence intensity during mechanical degradation of uranyl salts in the air, two triboluminescence spectral components have been recorded. The first peak is gas component (emitter is N_2, $N_2, C^3\Pi_u \rightarrow B^3\Pi_g$) [7] in the UV region, and the second is solid-state one (emitter is UO_2^{2+}, $^3\Pi_u \rightarrow {}^1\Sigma^+_g$) [10] coinciding with photoluminescence spectrum of crystals (see Fig. 2).

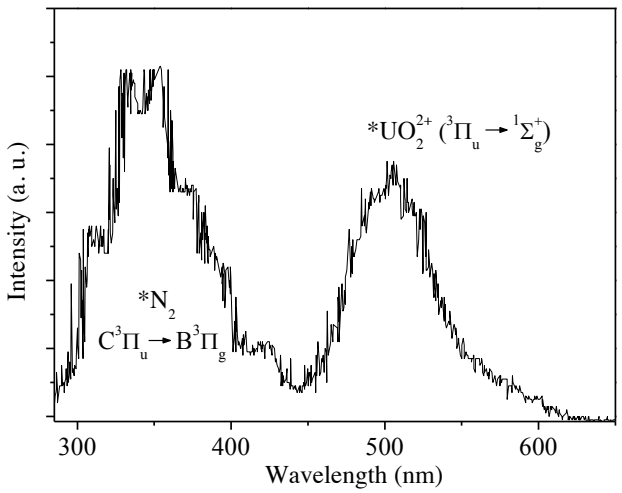

Figure 1. Triboluminescence spectrum of $UO_2(ClO_4)_2 \cdot 6H_2O$ at 77 K (spectrofluorimeter Aminco-Bowmen, $\Delta\lambda = 10$ nm)

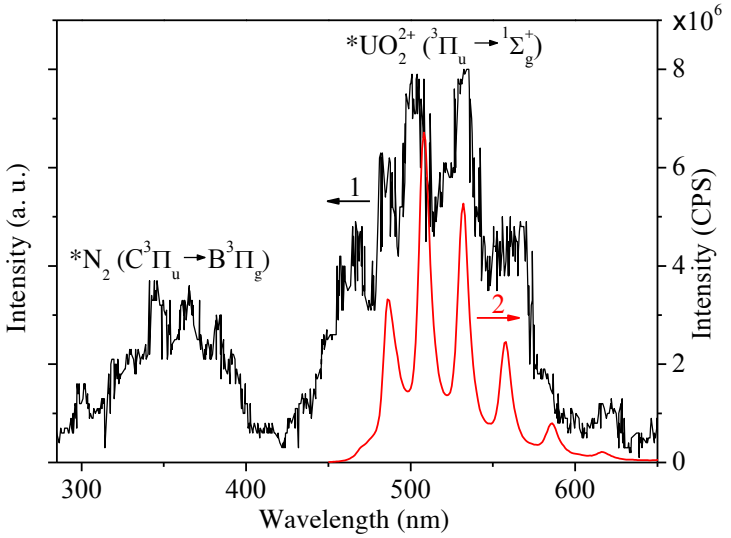

Figure 2. Spectra of crystals $UO_2(NO_3)_2 \cdot 6H_2O$: 1 – triboluminescence at 77 K (spectrofluorimeter Aminco-Bowmen, $\Delta\lambda$ = 5 nm); 2 – photoluminescence 77 K (spectrofluorimeter Fluorolog-3, λ_{ex}= 427 nm, $\Delta\lambda$= 1 nm)

After freezing of the uranyl salts, TL intensity was measured at 77-280 K at constant heating rate 7.2 K per min. For these salts, slight TL maximum at 80-90 K is observed without pre-excitation (see Fig. 3, curve 1). It is apparently due to the inherent emission (autoradioluminescence) possessed by these salts [11]. It is noteworthy that the TL peak is kept after repeated freezing and subsequent heating.

Then the crystals of uranyl salts were mechanically treated for a few minutes at 77 K and after and heated at the same constant rate 7.2 K per min. During heating at 80-90 K an increase of luminescence intensity up to 8-9 times (see Fig. 3, curve 2) is observed and compared with the luminescence without mechanical treatment. In addition, the luminescence intensity of the thermal peak depends on mechanical treatment time and increases with an increase at this time (see Fig. 4).

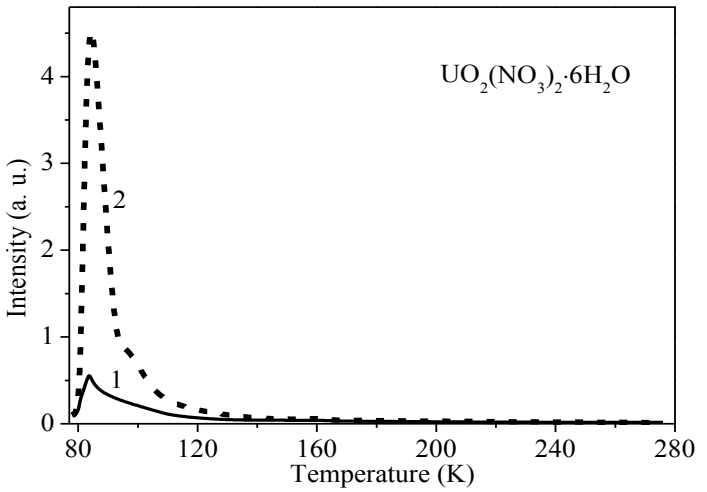

Figure 3. The luminescence intensity vs. temperature of uranyl nitrate before (1) and after (2) mechanical treatment. Heating rate constant was 7.2 K min^{-1}.

The position of the thermal peak *Tm*=83 K does not change (see Fig. 3). Apparently, these peaks occur due to release of the same energy traps.

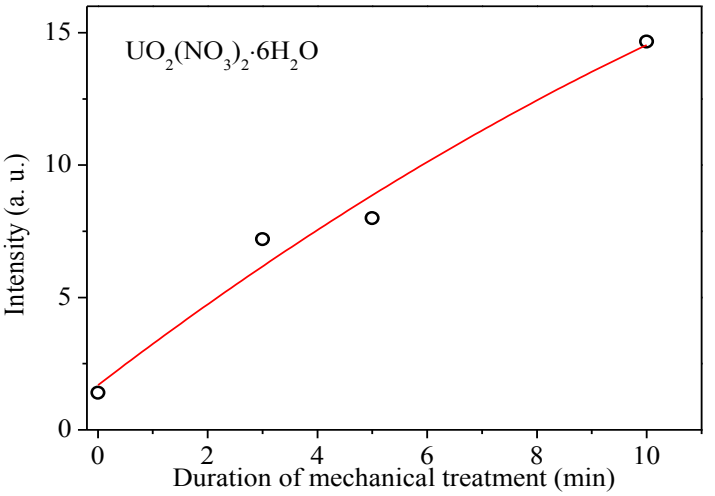

Figure 4. Relationship between luminescence intensity and mechanical treatment time of uranyl nitrate (T = 80-90 K).

The traps with certain depth are responsible for each TL maximum. The curve area is proportional to the population of the TL traps. The TL parameters (activation energy, frequency factor) is determined by the following formula [12]

$$E_{TL} \approx \frac{2kT_m^2}{\delta_m}, p_0 = \frac{\beta}{\delta_m}\exp\left(-\frac{T_m}{\delta_m}\right)$$

where T_m is temperature of the maximum peak (K), E_{TL} – activation energy (eV), k – Boltzmann constant ($8{,}613\cdot10^{-5}$ eV/K), δ_m – half-width of the peak, β – heating rate of the crystal. The calculated values of the activation energy and frequency factor were 0.21 eV and 10^{10} s^{-1}, respectively.

Acknowledgement

This work was supported by the Russian Foundation for Basic Research (project no. 14-02-31019 mol_a, no.14-02-97015).

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